

## Quantum-mechanical derivation of angular and torsional forces in well-bonded systems

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A quantum-mechanically based method of deriving real-space interatomic potential functions for covalently bonded systems, without broken bonds, is developed. The method focuses on the one-electron energy, which is modeled via a tight-binding Hamiltonian. The potentials are derived via a general formalism based on perturbation theory, using a starting state in which the electrons reside in bond orbitals. The perturbing terms correspond to overlap and Hamiltonian couplings between the bond orbitals and with other occupied and unoccupied states. The interactions are given in terms of simple trigonometric functions, and the parameters of the quantum-mechanical Hamiltonian. A major contribution to the angular forces comes from the overlap between occupied bonding orbitals. Examples are given for model Hamiltonians relevant to phosphorus, carbon, sulfur, and the ethane molecule. The functional forms of the derived potentials are generally similar in form to those assumed in simulations. However, the actual appearance of the potentials is sometimes quite different from that obtained by an empirical fitting to molecular properties. In addition, it is found that the "improper" torsion terms that are often included in polymer simulations can be replaced by angular terms that are much more physically transparent. [S0163-1829(96)02743-9]

### I. INTRODUCTION

Recent years have seen tremendous improvements in computing speed and capacity, which have rendered possible much larger and longer atomic-level simulation runs for properties of molecules and solids. These simulations require the use of rapid methods for evaluating the forces that enter Newton's equations, so that in most large-scale simulations, simple parametrized methods based on short-ranged real-space interatomic forces have been used. For covalent systems with conformational degrees of freedom, up to four-body or "torsional" interactions are typically used. Even for well-bonded systems, in which one does not have the difficulties of dealing with broken bonds, the forces are usually derived on the basis of an assumed functional form containing a large number of adjustable parameters. The parameters, which can number up to 1000 or more for a protein, are obtained by fitting to known molecular or solid-state properties. Because the functional form is assumed and the number of parameters is large, there is always a lingering uncertainty with regard to the accuracy of the simulations. In addition, the large number of adjustable parameters makes the generation of force laws for new systems time consuming.

The purpose of this paper is to provide a firmer theoretical foundation for the use of real-space force laws in simulations of well-bonded covalent systems, by developing a perturbative quantum-mechanical formalism for calculating them. I focus on the electronic band energy, for two reasons. First, since it depends on a solution of the Schrödinger equation for the electrons, it is the least well understood of the energy terms. Second, it is probably the dominant term in the angular and torsional forces, since electrostatic and fluctuating-dipole forces are not strongly angular in character. I describe the electronic-band energy via an electronic Hamiltonian based on tight-binding theory. This approach has previously proved of great utility in understanding structural and elastic

properties of transition metals and covalently bonded materials.

Several previous studies have treated the decomposition of the electronic band energy in tight-binding Hamiltonians into real-space interactions. For  $sp^3$ -bonded semiconductors, Harrison and Phillips<sup>1</sup> used a picture based on atom-centered hybrid orbitals with "frozen" orientations. In this picture, the interatomic bonding matrix elements are reduced as the bond angles change, causing the constituent hybrids to become misaligned in the bond, resulting in an angular term in the energy. This gives a good description of chemical trends in shear elastic constants in diamond-structure semiconductors. Subsequently, Harrison<sup>2</sup> presented an analysis for transition-metal compounds based on the "chemical grip." Here, the angular terms appear in fourth-order perturbation theory connecting the occupied orbitals to unoccupied ones. More recently, several analyses<sup>3-6</sup> have used the moments of the electronic density of states, together with an approximate dependence of the energy on these moments, to calculate the angular forces. Bond-order effects have also been calculated quantum mechanically<sup>7</sup> and invoked in empirical force methods.<sup>8,9</sup> However, there has been no corresponding analysis of the contribution of one-electron band effects to torsional forces within simple models such as those used here, although there have been several calculations for specific systems using other approaches.<sup>10</sup>

The approach that is used here, like Ref. 1, uses as a starting point a Hamiltonian including only couplings between different "lobes," whose symmetric linear combinations form bonding orbitals. This was denoted the "bond-orbital" approximation in Ref. 11. This approximation is suitable here because the systems of interest are well bonded. However, rather than using frozen atomic orbitals to construct the bond orbitals, I use bond orbitals that are oriented from one atom to another. This approach is advantageous for treating noncrystalline systems, because in these systems the choice of orientation for the frozen atomic orbitals is not

clear. Although this choice would not matter in an exact calculation, it does matter in an approximate calculation. For example, even in a perfect crystal, if one chooses an orientation for the atomic orbitals that is not suited to the crystal orientation, the bonds do not match up perfectly, and the energy in the bond-orbital approximation is found to be higher than it should be. The use of bond hybrids oriented according to the neighbor positions eliminates this ambiguity. The price paid for this simplification is that the bond orbitals emanating from a given atom become nonorthogonal when the bond angles deviate from their ideal values. A substantial part of this paper is devoted to treating this nonorthogonality, and I find that a major part of the angular interaction between bond orbitals may be attributed to the nonorthogonality. This does not contradict the results of Ref. 1; I believe that the energy of bond-angle deviations is physically the same in both pictures, but simply looks different because of the different choice of atomic-orbital basis. However, the present approach does allow for a very clear, systematic perturbation theory to be developed, which gives corrections to the picture of Ref. 1.

The calculation of the interactions proceeds via perturbation theory with respect to a starting Hamiltonian ( $\hat{H}_0$ ) that contains only noninteracting, orthogonal bond and antibond orbitals oriented between neighbors. The correction terms include bond-bond, bond-antibond, and antibond-antibond interactions, and nonorthogonality between different bond orbitals. Treatment up to fourth order yields both angular and torsional forces. These are expressed explicitly in terms of the electronic coupling terms in the Hamiltonian, and simple angular factors. This result implies that it may be possible to develop force laws with much fewer adjustable parameters than have typically been used, since the number of parameters in the electronic Hamiltonian is much smaller than the usual number of force parameters. I evaluate the forces for some simple model electronic Hamiltonians. The functional form of the angular dependence is generally similar to that assumed in most simulations. However, the actual plots can look quite different from the empirical potentials. In addition, the angular terms have a form which is general enough to subsume the effects of the ‘‘improper torsion,’’ or out-of-plane terms, which have been included in some previous simulations.<sup>12</sup> Thus it may be possible to simplify the treatment of these terms.

The organization of the remainder of the paper is as follows. Section II describes the general perturbative formalism, up to fourth order. Section III describes applications to simple types of bonding, including  $p$  bonding,  $sp^3$  bonding, and  $sp^2$  bonding. Applications are made to the structures of group V and VI elements, and a comparison is made to existing potentials for carbon. Section IV concludes with a discussion of prospects for including this basic physics in an empirically fitted force method.

## II. GENERAL FORMALISM

The Hamiltonian for the electronic-band energy, which I will first give in the absence of overlap (nonorthogonality), has the tight-binding form

$$\hat{H} = \sum_{ij} h_{ij} |i\rangle\langle j| + \sum_i \varepsilon_i |i\rangle\langle i|. \quad (1)$$

Here, the  $|i\rangle$  are localized basis orbitals, which are of  $p$  symmetry, or appropriately chosen  $s$ - $p$  hybrids, depending on the nature of the bonding. Each atom will contain several such basis orbitals, but they are not explicitly divided up into atomic groups here. The  $h_{ij} = \langle i|H|j\rangle$  are tight-binding couplings and the  $\varepsilon_i = \langle i|H|i\rangle$  are on-site energies. To obtain a starting point for calculating the interatomic potentials via perturbation theory, I assume that each basis orbital  $|i\rangle$  is strongly bonded to one and only one other basis orbital  $|i'\rangle$ ; this corresponds to the ‘‘bond-orbital’’ approximation.<sup>11</sup> It is assumed that  $|i\rangle$  and  $|i'\rangle$  ‘‘point’’ at each other, so that they are actually dependent on the atomic positions. Then the starting Hamiltonian is

$$\hat{H}_0 = \sum_i [h_{ii'}(|i\rangle\langle i'| + |i'\rangle\langle i|) + \varepsilon_i |i\rangle\langle i| + \varepsilon_{i'} |i'\rangle\langle i'|], \quad (2)$$

where the sum includes each pair only once. The eigenvalues of this Hamiltonian are straightforwardly obtained as  $\bar{\varepsilon} \pm \sqrt{h_{ii'}^2 + \delta\varepsilon^2}$ , where  $\bar{\varepsilon} = |\varepsilon_i + \varepsilon_{i'}|/2$  and  $\delta\varepsilon = |\varepsilon_i - \varepsilon_{i'}|/2$ . We denote the corresponding eigenvectors by  $|b_i\rangle$  (bonding) and  $|a_i\rangle$  (antibonding). In terms of these,  $\hat{H}_0$  takes the simple form

$$\hat{H}_0 = \sum_i [\varepsilon_{b,i} |b_i\rangle\langle b_i| + \varepsilon_{a,i} |a_i\rangle\langle a_i|]. \quad (3)$$

I assume that the bonding states are occupied and the antibonding states unoccupied. Thus the total energy of the system at this level is  $2\sum_i \varepsilon_{b,i}$ , where the factor of two that precedes the summation comes from the occupation of each bonding orbital by two electrons.

It is necessary to consider two types of corrections to this Hamiltonian. First, there are matrix elements coupling a given bonding or antibonding orbital to other bonding and antibonding orbitals. This correction has the form

$$\begin{aligned} \hat{H}_{\text{coup}} = & \sum'_{i,j} h_{ij}^{bb} |b_i\rangle\langle b_j| + h_{ij}^{ba} |b_i\rangle\langle a_j| \\ & + h_{ij}^{ab} |a_i\rangle\langle b_j| + h_{ij}^{aa} |a_i\rangle\langle a_j|, \end{aligned} \quad (4)$$

where the prime denotes that diagonal terms are omitted. Second, the bond orbitals are generally not orthogonal to each other.  $\hat{H}_{\text{coup}}$  is treated by perturbation theory, up to fourth order. The nonorthogonality is treated by use of the transformed Hamiltonian matrix  $(\hat{I} + \hat{S})^{-1/2} (\hat{H}_0 + \hat{H}_{\text{coup}}) (\hat{I} + \hat{S})^{-1/2}$ , where the matrix elements of  $\hat{S}$  are  $s_{ij}^{ba} = \langle b_i|a_j\rangle$ , etc., and the diagonal terms are subtracted off. (Note that here the ‘‘hat’’ notation corresponds to a collection of matrix elements, not the operator itself. Thus in the absence of orthogonality, one cannot square the matrix  $\hat{H}$  to obtain the square of the Hamiltonian.) The eigenvalues of the Hamiltonian, including overlap effects, are rigorously given as eigenvalues of this transformed Hamiltonian matrix.<sup>13</sup> The latter, in turn, is obtained by an expansion to the first and second order in  $\hat{S}$ . In the second-order part, we keep only the piece that includes  $\hat{H}_0$ , so that

only terms up to combined second order in  $\hat{H}_{\text{coup}}$  and  $\hat{S}$  are included. The end result is that the Hamiltonian matrix to be diagonalized has the form

$$\hat{H}_{\text{eff}} = \hat{H}_0 + \hat{H}_{\text{coup}} + \hat{H}_{\text{overlap}}, \quad (5)$$

where  $\hat{H}_{\text{overlap}} = -[\hat{S}(\hat{H}_0 + \hat{H}_{\text{coup}}) + (\hat{H}_0 + \hat{H}_{\text{coup}})\hat{S}]/2 + [(3/8)(\hat{S}^2\hat{H}_0 + \hat{H}_0\hat{S}^2) + (1/4)(\hat{S}\hat{H}_0\hat{S})]$ .

I now show that this expansion yields a real-space description of the bonding energy as a series of interatomic-potential functions. The expansion strategy, at first, is to keep all terms up to second order in  $\hat{H}_{\text{coup}}$  and  $\hat{S}$ . Thus the  $\hat{S}\hat{H}_0$  piece of  $\hat{H}_{\text{overlap}}$  is thus treated up to the second order and the remaining pieces are treated to the first order. The first-order contribution to the total energy from  $\hat{H}_{\text{coup}}$  vanishes, since the  $a$  orbitals are empty, and interactions between completely filled  $b$  orbitals do not change the total energy. The first-order contribution from  $\hat{H}_{\text{overlap}}$  is given by

$$\begin{aligned} E^{(1)} &= 2 \sum_i \langle b_i | \hat{H}_{\text{overlap}} | b_i \rangle \\ &= -2 \sum_{i,j} (h_{ij}^{bb} s_{ij}^{bb} + h_{ij}^{ba} s_{ij}^{ab}) \\ &\quad + 2 \sum_{i,j} [(s_{ij}^{bb})^2 \varepsilon_{b,i} + (3/4)(s_{ij}^{ba})^2 \varepsilon_{b,i} \\ &\quad + (1/4)(s_{ij}^{ba})^2 \varepsilon_{a,j}], \end{aligned} \quad (6)$$

where, as above, the factor of two that precedes each summation comes from the spin degeneracy. In this result, the diagonal terms are to be included. The energy now has the form of a sum of interactions between bonds:

$$\Delta E_{\text{overlap}}^{(1)} = 1/2 \sum_{i \neq j} V_{ij}^{(1)} + (i=j \text{ terms}), \quad (7)$$

where

$$\begin{aligned} V_{ij}^{(1)} &= -4(h_{ij}^{bb} s_{ij}^{bb} + h_{ij}^{ba} s_{ij}^{ab}) + 2(s_{ij}^{bb})^2 (\varepsilon_{b,i} + \varepsilon_{b,j}) \\ &\quad + (3/2)[(s_{ij}^{ba})^2 \varepsilon_{b,i} + (s_{ij}^{ab})^2 \varepsilon_{b,j}] \\ &\quad + (1/2)[(s_{ij}^{ba})^2 \varepsilon_{a,j} + (s_{ij}^{ab})^2 \varepsilon_{a,i}]. \end{aligned} \quad (8)$$

[The second term in Eq. (7) simply contributes a shift in the bond energy which does not contribute to the angular or torsional forces.] The second-order treatment of the  $\hat{H}_{\text{coup}}$  and  $\hat{S}\hat{H}_0 + \hat{H}_0\hat{S}$  terms gives the following result:

$$\begin{aligned} \Delta E^{(2)} &= 2 \sum_{i,j} \langle b_i | \hat{H}_{\text{coup}} - (\hat{S}\hat{H}_0 + \hat{H}_0\hat{S})/2 | a_j \rangle^2 / (\varepsilon_{b,i} - \varepsilon_{a,j}) \\ &= 2 \sum_{i,j} [\tilde{h}_{ij}^{ba}]^2 / (\varepsilon_{b,i} - \varepsilon_{a,j}), \end{aligned} \quad (9)$$

where

$$\tilde{h}_{ij}^{ba} = h_{ij}^{ba} - s_{ij}^{ba} (\varepsilon_{b,i} + \varepsilon_{a,j})/2. \quad (10)$$

The corresponding bond-bond interaction is

$$V_{ij}^{(2)} = 2[\tilde{h}_{ij}^{ba}]^2 / (\varepsilon_{b,i} - \varepsilon_{a,j}) + (i \leftrightarrow j). \quad (11)$$

In the results (8) and (11), one obtains an angular interaction if  $i$  and  $j$  correspond to different ligand bonds on the same atom. One obtains a torsional interaction if  $i$  and  $j$  correspond to ligand bonds on different atoms that are connected by an axial bond.

We shall see later that the description of some angular and torsional interactions necessitates the inclusion of ‘‘extra’’ orbitals in addition to those formally involved in the bonding. Their inclusion requires going up to fourth-order perturbation theory, where the perturbation is  $\hat{U} = \hat{H}_{\text{coup}} - [\hat{S}(\hat{H}_0 + \hat{H}_{\text{coup}}) + (\hat{H}_0 + \hat{H}_{\text{coup}})\hat{S}]/2$ . We define  $\hat{U}$  to include only the off-diagonal part of this expression. This is because it simplifies the calculation, and we have found that angular dependences obtained using the diagonal part always show up in higher orders of perturbation theory than in calculations based on the off-diagonal part. Terms of up to fourth order can also be obtained by treating the second-order part of  $\hat{H}_{\text{eff}}$  to second order; however, these terms are found to have the same angular dependence as lower-order terms.

Fourth-order perturbation theory can become rather unwieldy, so I now give a derivation which renders the ‘‘book-keeping’’ simple. I set up the calculation in terms of a Green’s function  $\hat{G}$  defined by

$$\hat{G}(z) = 1/(z - \hat{H}_0 - \hat{U}). \quad (12)$$

By assumption, the filled bonding orbitals are well removed in energy from the others. Assume at first that the extra orbitals are empty, and thus act only by perturbing the occupied orbitals. Define  $C$  to be a contour surrounding all of the occupied bonding orbitals and none of the empty remaining ones. Then one sees readily from the Cauchy integral formula that the total bonding energy is  $2(1/2\pi i) \oint_C \text{Tr} \hat{G}(z) dz$ , where the first ‘‘2’’ accounts for the spin degeneracy. The point is that  $\hat{G}(z)$  is well-behaved along the contour, and can thus be expanded as a power series in the perturbing terms. We write  $\hat{U} = \sum_{\mu, \nu} \tilde{h}_{\mu\nu} |\mu\rangle \langle \nu|$ , where the states  $\mu$  comprise the collection of bonding ( $b$ ), antibonding ( $a$ ), and ‘‘extra’’ ( $e$ ) orbitals. By assumption  $\hat{H}_0$  is diagonal, so that  $\hat{G}_0(z) = \sum_{\mu} (z - \varepsilon_{\mu})^{-1} |\mu\rangle \langle \mu|$ . Expanding to fourth order in  $\hat{U}$ , we obtain

$$\begin{aligned} \hat{G}(z) &= \hat{G}_0(z) + \hat{G}_0(z) \hat{U} \hat{G}_0(z) + \hat{G}_0(z) \hat{U} \hat{G}_0(z) \hat{U} \hat{G}_0(z) \\ &\quad + \hat{G}_0(z) \hat{U} \hat{G}_0(z) \hat{U} \hat{G}_0(z) \hat{U} \hat{G}_0(z) \\ &\quad + \hat{G}_0(z) \hat{U} \hat{G}_0(z) \hat{U} \hat{G}_0(z) \hat{U} \hat{G}_0(z) \hat{U} \hat{G}_0(z), \end{aligned} \quad (13)$$

so that

$$\begin{aligned} E^{(2)} &= (\pi i)^{-1} \sum_{\mu, \nu} \oint_C z \tilde{h}_{\mu\nu} \tilde{h}_{\nu\mu} \\ &\quad \times [(z - \varepsilon_{\mu})(z - \varepsilon_{\nu})(z - \varepsilon_{\mu})]^{-1} dz, \end{aligned} \quad (14)$$

$$E^{(3)} = (\pi i)^{-1} \sum_{\mu, \nu, \eta} \oint_C z \tilde{h}_{\mu\nu} \tilde{h}_{\nu\eta} \tilde{h}_{\eta\mu} [(z - \varepsilon_\mu)(z - \varepsilon_\nu) \times (z - \varepsilon_\eta)(z - \varepsilon_\mu)]^{-1} dz, \quad (15)$$

and

$$E^{(4)} = (\pi i)^{-1} \sum_{\mu, \nu, \eta, \gamma} \oint_C z \tilde{h}_{\mu\nu} \tilde{h}_{\nu\eta} \tilde{h}_{\eta\gamma} \tilde{h}_{\gamma\mu} [(z - \varepsilon_\mu)(z - \varepsilon_\nu) \times (z - \varepsilon_\eta)(z - \varepsilon_\gamma)(z - \varepsilon_\mu)]^{-1} dz. \quad (16)$$

I consider  $E^{(2)}$  first. For the assumed case in which the  $e$  orbitals are empty, the nonvanishing terms are those involving a  $b$  orbital and an  $e$  orbital; those not containing any  $b$  orbitals vanish because the corresponding integrand has no singularities inside the contour. Equation (14) then yields

$$\begin{aligned} E^{(2)} &= (\pi i)^{-1} \text{Tr} \hat{U}_{be} \hat{U}_{eb} \oint_C z [(z - \varepsilon_b)(z - \varepsilon_e)]^{-1} \\ &\quad \times [(z - \varepsilon_b)^{-1} + (z - \varepsilon_e)^{-1}] \\ &= 2 \text{Tr} \hat{U}_{be} \hat{U}_{eb} (\varepsilon_b - \varepsilon_e)^{-1} \\ &= 2 \sum \tilde{h}_{im}^{be} \tilde{h}_{mi}^{eb} (\varepsilon_b - \varepsilon_e)^{-1}, \end{aligned} \quad (17)$$

which is the usual second-order perturbation theory expression. For the case of filled  $e$  orbitals, we note that by assumption  $\text{Tr}(\hat{H}_0 + \hat{U}) = \text{Tr} \hat{H}_0$ , since  $\hat{U}$  is by assumption off diagonal. This means that the sum of all of the eigenvalues is unaffected by  $\hat{U}$ . Then we can write the sum of the energy changes of the occupied bonding and extra states as minus the energy change of the empty antibonding states. In other words, we take the above expression, interchange  $a$  and  $b$  everywhere, and put a minus sign in front. Thus, for filled  $e$  states,

$$E^{(2)} = 2 \sum_e \tilde{h}_{im}^{ae} \tilde{h}_{mi}^{ea} (\varepsilon_e - \varepsilon_a)^{-1}. \quad (18)$$

In  $E^{(3)}$ , the nonvanishing pieces are those which contain some  $b$  terms and some of the others as well. This holds because the pieces which contain no  $b$  terms vanish since the corresponding integrand has no singularities inside the contour: the pieces which contain only  $b$  terms vanish because the integrand is of the form  $z(z - \varepsilon_b)^{-3}$ , and one readily shows that its integral vanishes. For the case of angular interactions influenced by the  $e$  orbitals, one readily sees that one of  $\mu$ ,  $\nu$ , and  $\eta$  must be an  $e$  orbital and the remaining two must be either both  $b$  orbitals or one  $b$  orbital and one  $a$  orbital.

Using this result in Eq. (15), we obtain

$$\begin{aligned} E^{(3)} &= (\pi i)^{-1} \text{Tr} \hat{U}_{be} \hat{U}_{eb} \hat{U}_{bb} \oint_C z [(z - \varepsilon_b)^2 (z - \varepsilon_e)]^{-1} \\ &\quad \times [2(z - \varepsilon_b)^{-1} + (z - \varepsilon_e)^{-1}] \\ &\quad + 2(\pi i)^{-1} \text{Tr} \hat{U}_{be} \hat{U}_{ea} \hat{U}_{ab} \oint_C z [(z - \varepsilon_b)(z - \varepsilon_e) \\ &\quad \times (z - \varepsilon_a)]^{-1} [(z - \varepsilon_b)^{-1} + (z - \varepsilon_e)^{-1} + (z - \varepsilon_a)^{-1}] \\ &= -2 \text{Tr} \hat{U}_{be} \hat{U}_{eb} \hat{U}_{bb} (\varepsilon_b - \varepsilon_e)^{-2} \\ &\quad + 4 \text{Tr} \hat{U}_{be} \hat{U}_{ea} \hat{U}_{ab} (\varepsilon_b - \varepsilon_e)^{-1} (\varepsilon_b - \varepsilon_a)^{-1}. \end{aligned} \quad (19)$$

In terms of an angular potential defined between bonds  $|i\rangle$  and  $|j\rangle$  on atom  $m$ , we have

$$\begin{aligned} V_{ij}^{(3)} &= 2 \left[ - \sum_e \tilde{h}_{im}^{be} \tilde{h}_{mj}^{eb} \tilde{h}_{ji}^{bb} (\varepsilon_b - \varepsilon_e)^{-2} + 2 \sum_e \tilde{h}_{im}^{be} \tilde{h}_{mj}^{ea} \tilde{h}_{ji}^{ab} \right. \\ &\quad \left. \times (\varepsilon_b - \varepsilon_e)^{-1} (\varepsilon_b - \varepsilon_a)^{-1} \right] + (i \leftrightarrow j). \end{aligned} \quad (20)$$

For the case of filled  $e$  orbitals, I obtain

$$\begin{aligned} V_{ij}^{(3)} &= 2 \left[ \sum_e \tilde{h}_{im}^{ae} \tilde{h}_{mj}^{ea} \tilde{h}_{ji}^{aa} (\varepsilon_e - \varepsilon_a)^{-2} + 2 \sum_e \tilde{h}_{im}^{ae} \tilde{h}_{mj}^{eb} \tilde{h}_{ji}^{ba} \right. \\ &\quad \left. \times (\varepsilon_e - \varepsilon_a)^{-1} (\varepsilon_b - \varepsilon_a)^{-1} \right] + (i \leftrightarrow j). \end{aligned} \quad (21)$$

These results will be used to discuss effects of the extra orbitals on bond angles, in the next section.

I now turn to  $E^{(4)}$ . As for  $E^{(3)}$ , the nonzero pieces contain some  $b$  terms and some of the others as well. For torsional forces to be present, two of the states  $\mu$ ,  $\nu$ ,  $\eta$ , and  $\gamma$  must be bonding or antibonding orbitals between the two axial-bond atoms and ligand neighbors. For the  $e$  to states to come into play, it turns out that two of the states  $\mu$ ,  $\nu$ ,  $\eta$ , and  $\gamma$  must also be  $e$  states residing on the two axial-bond atoms, and the coupling between these states must be present. For  $d$  orbitals, this is the only way to get sufficiently rapid angular variations of the torsional potential; for  $p$  orbitals, this is required to obtain a mediated interaction between the two ligands. In summary, of the four states  $\mu$ ,  $\nu$ ,  $\eta$ , and  $\gamma$ , at least one must be a bonding ligand orbital, another must be a bonding or antibonding ligand orbital, and the remaining two must be  $e$  orbitals residing on the two atoms.

Using these results in Eq. (16), we obtain

$$\begin{aligned} E^{(4)} &= (\pi i)^{-1} \text{Tr} \hat{U}_{be} \hat{U}_{ee} \hat{U}_{eb} \hat{U}_{bb} \oint_C 2z [(z - \varepsilon_b)^2 \\ &\quad \times (z - \varepsilon_e)^2]^{-1} [(z - \varepsilon_b)^{-1} + (z - \varepsilon_e)^{-1}] \\ &\quad + 2(\pi i)^{-1} \text{Tr} \hat{U}_{be} \hat{U}_{ee} \hat{U}_{ea} \hat{U}_{ab} \oint_C z [(z - \varepsilon_b)(z - \varepsilon_e)^2 \\ &\quad \times (z - \varepsilon_a)]^{-1} [(z - \varepsilon_b)^{-1} + 2(z - \varepsilon_e)^{-1} + (z - \varepsilon_a)^{-1}]. \end{aligned} \quad (22)$$

Performing the integrals, we obtain

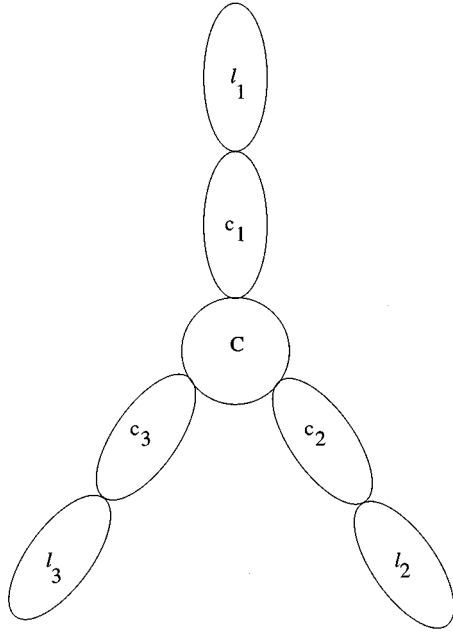


FIG. 1. Schematic of central atom  $C$ , with orbitals  $c_i$ , surrounded by ligand orbitals  $l_i$ .

$$E^{(4)} = -4 \text{Tr} \hat{U}_{be} \hat{U}_{ee} \hat{U}_{eb} \hat{U}_{bb} (\varepsilon_b - \varepsilon_e)^{-3} + 4 \text{Tr} \hat{U}_{be} \hat{U}_{ee} \hat{U}_{ea} \hat{U}_{ab} (\varepsilon_b - \varepsilon_e)^{-2} (\varepsilon_b - \varepsilon_a)^{-1}. \quad (23)$$

The torsional potential between ligand bonds  $|i\rangle$  on atom  $m$  and  $|j\rangle$  on atom  $n$  is then

$$V_{ij}^{(4)} = 4 \left[ - \sum_e \tilde{h}_{im}^{be} \tilde{h}_{mn}^{ee} \tilde{h}_{nj}^{eb} \tilde{h}_{ji}^{bb} (\varepsilon_b - \varepsilon_e)^{-3} + \sum_e \tilde{h}_{im}^{be} \tilde{h}_{mn}^{ee} \tilde{h}_{nj}^{ea} \tilde{h}_{ji}^{ab} (\varepsilon_b - \varepsilon_e)^{-2} (\varepsilon_b - \varepsilon_a)^{-1} + (i \leftrightarrow j) \right]. \quad (24)$$

For filled  $e$  states, I obtain

$$V_{ij}^{(4)} = 4 \left[ - \sum_e \tilde{h}_{im}^{ae} \tilde{h}_{mn}^{ee} \tilde{h}_{nj}^{ea} \tilde{h}_{ji}^{aa} (\varepsilon_e - \varepsilon_a)^{-3} + \sum_e \tilde{h}_{im}^{ae} \tilde{h}_{mn}^{ee} \tilde{h}_{nj}^{eb} \tilde{h}_{ji}^{ba} (\varepsilon_e - \varepsilon_a)^{-2} (\varepsilon_b - \varepsilon_a)^{-1} \right] + (i \leftrightarrow j). \quad (25)$$

This is the result underlying the specific calculations of torsional forces in the following section.

### III. APPLICATIONS

In this section, I derive the geometric form of the forces calculated with the above formalism, for some simple standard cases, using a ‘‘bare-bones’’ model of the electronic structure, intended to exemplify certain ideal types of bonding. These relatively simple calculations illustrate the basic principles which will be needed for more complex applications.

#### A. Angular forces

Consider first the angular forces for the case of a  $p$ -type atom surrounded by three neighbors that are equivalent to it. As illustrated in Fig. 1, I consider a central atom ‘‘ $C$ ’’ having three  $p$ -type basis orbitals  $|c_i\rangle$  pointing directly at its neighbors. In turn, each neighbor has a ligand orbital  $|l_i\rangle$  strongly bonded to  $|c_i\rangle$ . The coupling between the lobes in each bonding and antibonding orbital is  $-h$ . Since the ligands are equivalent to the central atom, the bonding and antibonding orbitals have amplitudes  $\pm 1/\sqrt{2}$  on each bond hybrid. The overlap and Hamiltonian matrix elements between the hybrids are readily obtained from the usual Slater-Koster analysis.<sup>14</sup> We ignore direct interactions between lobes centered on distinct ligand atoms of a central atom, since the distance between these atoms will generally be much larger than the bond length. In addition, we ignore interatomic overlap for simplicity; it changes the magnitude of the interactions, but not their functional form. Denoting the overlap between lobes on the same atom by  $s(\theta) = \cos\theta$ , and the intra-atomic Hamiltonian matrix elements between lobes by  $\varepsilon(\theta) = \varepsilon_p \cos\theta$  (where  $\varepsilon_p$  is the  $p$ -orbital energy), we have

$$\varepsilon_{b,i} = \varepsilon_p - h, \quad \varepsilon_{a,i} = \varepsilon_p + h, \quad (26)$$

$$s_{ij}^{bb} = (1/2)s(\theta_{ij}) = s_{ij}^{ba} = s_{ij}^{ab}, \quad (27)$$

$$h_{ij}^{bb} = (1/2)\varepsilon(\theta_{ij}) - hs(\theta_{ij}), \quad (28)$$

$$h_{ij}^{aa} = (1/2)\varepsilon(\theta_{ij}) + hs(\theta_{ij}), \quad (29)$$

and

$$h_{ij}^{ba} = (1/2)\varepsilon(\theta_{ij}) = h_{ij}^{ab}. \quad (30)$$

Thus  $\tilde{h}_{ij}^{ba}$  [cf. Eq. (10)] vanishes, and so does  $V^{(2)}$ , according to Eq. (11). Then, using Eq. (8), we obtain

$$V(\theta) = V^{(1)}(\theta) = (h/2)s(\theta)^2. \quad (31)$$

Thus the potential has a simple  $(\cos)^2$  form, which minimizes at  $90^\circ$ . The underlying physics is simply that at  $90^\circ$ , the orbitals can bond independently and each form a full bond, which minimizes the bond energy.

The closest physical realizations of this model are the group V elements phosphorus and arsenic. (For nitrogen, the bonding is molecular, and for the elements farther down in group V, the tight-binding approximation becomes less reliable.) The geometric properties of the observed structures here and below are taken from Ref. 15, unless otherwise noted. Both phosphorus and arsenic take on a large variety of crystal structures. For phosphorus, the observed bond angles range from  $95^\circ$  to  $105^\circ$ . For arsenic in its ‘‘ $\alpha$ ’’ structure, the bond angle is  $95^\circ$ . So the basic form of the calculated potential seems to be credible. I shall now show that the systematic deviation in the direction of larger bond angles is associated partly with hybridization effects arising from either occupied  $3s$ - or unoccupied  $4s$  orbitals, or both. I calculate these with the help of the third-order perturbation theory described above. Consider Eqs. (20) and (21), where the extra state is an  $s$  state residing on the central atom. As men-

tioned above,  $\tilde{h}_{ji}^{ba}$  vanishes, so we only need to consider the first term in each of these equations. Since interatomic overlap is ignored,  $\tilde{h}_{im}^{be} = -\tilde{h}_{im}^{ae} = -(1/\sqrt{2})h_{sp\sigma}$ , where  $-h_{sp\sigma}$  is the coupling between the appropriately oriented  $p$  state on a neighboring atom and the  $s$  state on the central atom (the phases here correspond to a convention in which both the bonding and antibonding orbitals have positive phases on the central atom). One readily sees that  $\tilde{h}_{ji}^{bb} = -\tilde{h}_{ji}^{aa} = (-h/2)\cos\theta$ . Then the third-order contribution to the bond-angle potential is

$$V_{ij}^{(3)} = hh_{4sp\sigma}^2 \cos\theta / (\varepsilon_p - h - \varepsilon_{4s})^2 + hh_{3sp\sigma}^2 \cos\theta / (\varepsilon_{3s} - h - \varepsilon_p)^2. \quad (32)$$

This term will tend to favor larger bond angles, with the equilibrium angle being determined by a combination of this potential and that given by Eq. (31). Assuming that the hybridization effects are small, one finds the change in equilibrium bond angle,  $\Delta\theta$ , induced by this term to be approximately  $[h_{4sp\sigma}/(\varepsilon_p - h - \varepsilon_{4s})]^2 + [h_{3sp\sigma}/(\varepsilon_{3s} - h - \varepsilon_p)]^2$ . We do not have precise estimates for all of these parameters. However, approximate values  $h_{3sp\sigma} = 2.8$  eV and  $h = 4.9$  eV, as well as  $\varepsilon_p - \varepsilon_{3s} = 8.8$  eV can be obtained from the ‘‘Solid State Table of the Elements,’’ in Ref. 16. This gives  $\Delta\theta = 0.04$  rad =  $2.3^\circ$  for the  $3s$  terms. The effect from the  $4s$  states is likely to be larger, since their spatial extent is larger than that of the  $3s$  states, and  $\varepsilon_{4s} - \varepsilon_p$  is probably less than the  $p$ -binding energy, which is 8.3 eV. Thus the combination of these two terms is likely to give a bond-angle expansion effect comparable to the observed one.

Consider now the case of an  $sp^3$  atom surrounded by four neighbors that are equivalent to it. Each of the hybrid orbitals has  $\sqrt{1/4}$   $s$  amplitude and  $\sqrt{3/4}$   $p$  amplitude. As in the above case, the coupling between the lobes of the bonding and antibonding orbitals is  $-h$ , and the bonding and antibonding orbitals have amplitudes  $\pm 1/\sqrt{2}$  on each bond hybrid. In this case we have  $s(\theta) = [1/4 + (3/4)\cos\theta]$  and  $\varepsilon(\theta) = [\varepsilon_s/4 + (3/4)\varepsilon_p\cos\theta]$ . Noting that  $(\varepsilon_{bi} + \varepsilon_{ai})/2 = \varepsilon(0)$ , we have  $\tilde{h}_{ij}^{ba} = (1/2)[\varepsilon(\theta) - \varepsilon(0)s(\theta)] = (-3/16)\Delta\varepsilon(1 - \cos\theta)$ , where  $\Delta\varepsilon = (\varepsilon_p - \varepsilon_s)/2$  (not the same as  $\delta\varepsilon$ ). Then, using Eqs. (8) and (11), we obtain

$$V(\theta) = V^{(1)}(\theta) + V^{(2)}(\theta) = (h/2)s(\theta)^2 + (3/4)\Delta\varepsilon s(\theta)[1 - \cos\theta] - 2(3/16)^2(\Delta\varepsilon^2/h)[1 - \cos\theta]^2, \quad (33)$$

For the parallel case of  $sp^2$  bonding, we obtain

$$V(\theta) = (h/2)s(\theta)^2 + (8/9)\Delta\varepsilon s(\theta)[1 - \cos\theta] - 2(2/9)^2(\Delta\varepsilon^2/h)[1 - \cos\theta]^2, \quad (34)$$

where in this case  $s(\theta) = [1/3 + (2/3)\cos\theta]$ ,  $\varepsilon(\theta) = [\varepsilon_s/3 + (2/3)\varepsilon_p\cos\theta]$ , and  $\tilde{h}_{ij}^{ba} = (-2/9)\Delta\varepsilon(1 - \cos\theta)$ .

In both of these potentials, the first term is roughly consistent with what has been assumed in most simulations. Depending only on  $h$ , it appears to be directly analogous to the results of Ref. 1 (for the case of elemental semiconductors). In both  $sp^3$  and  $sp^2$  configurations,  $s(\theta)$  vanishes at the stable bond angle  $\theta_0$  (109.5 in  $sp^3$  and 120 in  $sp^2$ ), so that

this term of the potential has a quadratic minimum at the observed bond angle. This effect may be thought of as minimizing the overlap repulsion between the bond orbitals. Turning to the second term, we note that in each of the potentials  $s(\theta)$  is decreasing at  $\theta_0$ , and  $[1 - \cos\theta]$  is positive. Then this term has the effect of attempting to open the bonds. I will call it the ‘‘linear’’ term, since it is linear in  $s(\theta)$ . The origin of this term may be understood by considering a pair of the bonding orbitals pointing out of the central atom. Because  $\Delta\varepsilon > 0$ , the wave function built out of these orbitals will have a lower energy if their interference is such as to maximize the  $s$  component. Since both of the bond orbitals are formally filled, both symmetric and antisymmetric combinations of the bonding orbitals will be occupied (here ‘‘symmetric’’ is measured with respect to the atom, not the bond centers). In the symmetric combination, the  $s$  part is enhanced, while in the antisymmetric combination it is suppressed. Because of the nonorthogonality of the two bond orbitals, the symmetric and antisymmetric states are normalized by overlap factors  $1/[1 + (1/2)s(\theta)]$  and  $1/[1 - (1/2)s(\theta)]$ , respectively. Thus the  $s$  contribution in the bonding orbital will be enhanced if  $s(\theta)$  is negative, which corresponds to an increased bond angle. This explains in a rough way the origin of the linear term. The third term in Eqs. (33) and (34) is smaller than the others by roughly an order of magnitude, even for the largest values of  $\delta\varepsilon$  that are consistent with a nonzero band gap.

The form of this potential is compared with some existing potentials for carbon in Fig. 2(a). The present BO (‘‘bond-orbital’’) potential is calculated with parameters taken from Ref. 16. The ‘‘KS’’ potential is derived by Khor and Das Sarma<sup>17</sup> from a bond-order analysis using a cosine angular form, and has been used for calculations of condensed-matter properties. The WKNC potential (Weiner, Kollmann, Nguyen, and Case<sup>12</sup>) is a quadratic fit to the vibrational data. It has been derived for protein simulations. The main difference between the present potential and the others is that in the present case the minimum is pushed out to  $180^\circ$ . Note that this is not inconsistent with the observed bond angles of  $109.5^\circ$ , since these are the largest that can be achieved with fourfold coordination.

Figure 2(b) shows the BO potential for  $sp^2$  carbon. As in the  $sp^3$  case, there is an outward force at the observed bond angle,  $120^\circ$  in this case. This force may be related to the ‘‘improper torsion’’ terms that have been introduced in some protein simulations.<sup>12</sup> These are included because angular forces that have a minimum at  $120^\circ$  result in vanishing frequencies for the out-of-plane vibrational modes, in the sense that the distortion energy is proportional to  $\chi^4$ , where  $\chi$  is the out-of-plane angle. This may be seen as follows. As illustrated in Fig. 3, the change in the bond angle  $\Delta\theta$  induced by  $\chi$  is an even function of  $\chi$ , and therefore must be proportional to  $\chi^2$  for small  $\chi$ . If the angular potential is minimized at the observed angle, then the distortion energy is proportional to  $\Delta\theta^2$ , or to  $\chi^4$ . This has motivated the use of explicit terms associated with the out-of-plane angle. However, the present BO potentials provide a much simpler route to the out-of-plane energy. Since the angular potential is not minimized at the observed angle, the distortion energy is proportional to  $\Delta\theta$ , or to  $\chi^2$ , as it should be. Thus a nonzero out-of-plane vibrational energy is obtained simply by the form of

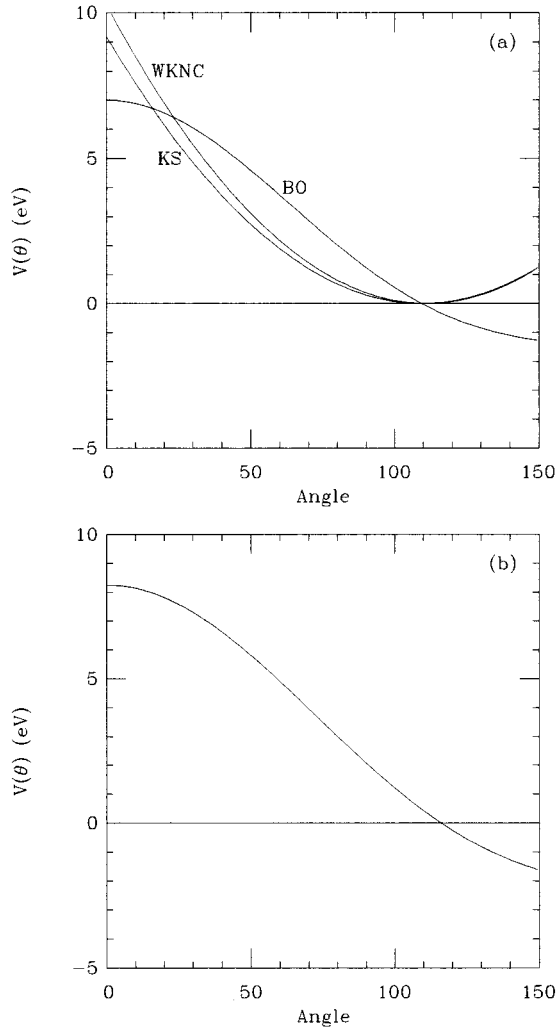


FIG. 2. Angular potentials for  $sp^3$  (a) and  $sp^2$  (b) carbon. ‘‘BO’’ denotes the potential obtained from the present analysis using bond-orbital approximation. Comparisons in (a) are taken from Refs. 12 and 17.

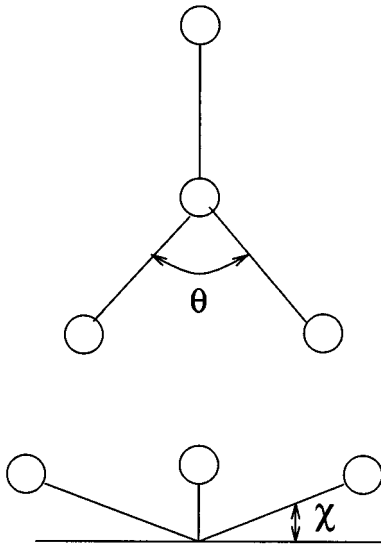


FIG. 3. Schematic of ‘‘improper torsion’’ terms.

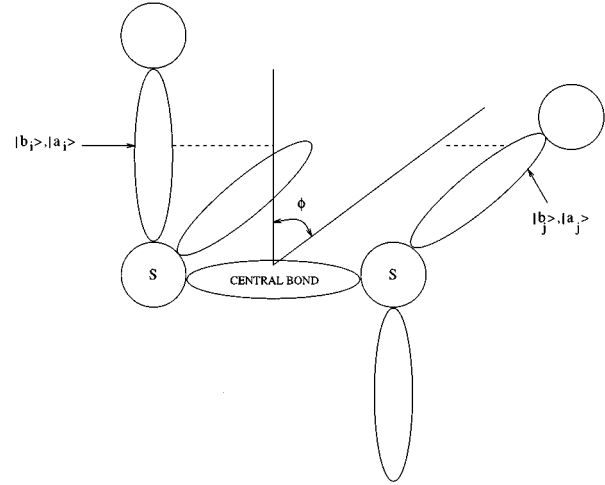


FIG. 4. Illustration of torsional potential calculation without extra orbitals.

the angular terms. Note that the magnitude of this effect is proportional to the difference between the  $s$ - and  $p$ -single-site energies in the present model [cf. Eq. (34)].

### B. Torsional forces

To isolate the torsional forces, we focus on the case where the bond orbitals point in orthogonal directions; this corresponds to bond angles of  $90^\circ$  for  $p$  bonding, and  $109.5^\circ$  for  $sp^3$  bonding. Again, we ignore the interatomic overlap for simplicity; since the interatomic overlap have the same angular dependence as the Hamiltonian couplings, this will not change the angular form of the potentials. Thus,  $V_{ij}^{(1)}=0$  according to Eq. (8). With all atoms equivalent,  $V^{(2)}$  [cf. Eq. (11)] reduces to

$$V_{ij}^{(2)} = 4(h_{ij}^{ba})^2 / (\varepsilon_b - \varepsilon_a). \quad (35)$$

Here,  $i$  and  $j$  correspond to ‘‘back’’ bonds of distinct atoms, as illustrated in Fig. 4. In terms of the torsional angle  $\phi$  about the central bond axis,  $h_{ij}^{ba} = -(1/2)h_{pp\pi}\cos\phi$  for pure  $p$  orbitals and

$$h_{ij}^{ba} = -(1/8)h_{ss\sigma} + (1/4\sqrt{3})h_{sp\sigma} - (1/24)h_{pp\sigma} - (1/3)h_{pp\pi}\cos\phi \quad (36)$$

for  $sp^3$  orbitals. Here I use the convention that all of the ‘‘Slater-Koster’’ couplings are positive in sign. In terms of these parameters, the interaction between the two lobes comprising a bond is given by  $-h = -(1/4)h_{ss\sigma} - (\sqrt{3}/2)h_{sp\sigma} - (3/4)h_{pp\sigma}$ . Then the torsional potential has the form

$$V(\phi) = -(h_{pp\pi}^2/2h)\cos^2\phi \quad (p \text{ orbitals}),$$

$$V(\phi) = -2[(1/8)h_{ss\sigma} - (1/4\sqrt{3})h_{sp\sigma} - (1/24)h_{pp\sigma} + (1/3)h_{pp\pi}\cos\phi]^2/h \quad (sp^3 \text{ orbitals}). \quad (37)$$

In the case of  $p$  bonding, the simple  $\cos^2$  behavior gives equal energy minima at  $0$  and  $180^\circ$ . In  $sp^3$  bonding, the

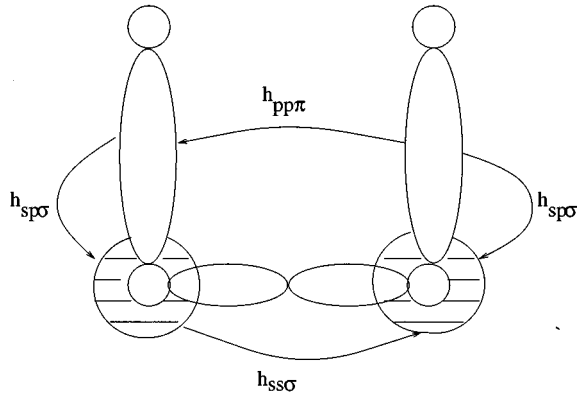


FIG. 5. Illustration of calculation of torsional potential using extra orbitals.

angular dependence includes both  $\cos$  and  $\cos^2$  terms. The minimum at  $0^\circ$  is deeper than that at  $180^\circ$ .

However, application of these potentials to the group V and IV elements treated in the preceding section gives a vanishing result for the energy barrier as a function of joint rotation of all of the bonds on one atom about to the bond axis. This is because the contributions from different torsional terms (four in the case of group V and nine in the case of group IV) interfere, so that their sum is constant as a function of the rotation angle. Thus we cannot use these idealized potentials to explain the observed torsional angles. It is then necessary to include contributions from other “extra” states that are not formally involved in the bonding. One then needs the fourth-order perturbation theory, as summarized in Eqs. (24) and (25).

In the case of phosphorus, these extra states should be the occupied  $3s$  shell or the unoccupied  $4s$  shell. This calculation is illustrated in Fig. 5, for the  $4s$  case. In Eq. (24),  $h_{im}^{be} = h_{nj}^{be} = -h_{im}^{ae} = -h_{nj}^{ae} = -(1/\sqrt{2})h_{sp}$  (the relative minus sign for the  $a$  couplings results because of the negative sign on the orbital on the neighbor atom),  $h_{mn}^{ee} = -h_{ss\sigma}$ , and  $h_{ji}^{bb} = h_{ji}^{ba} = -(1/2)h_{pp\pi}\cos\phi$ . Then,

$$V(\phi) = -2h_{sp\sigma}^2 h_{ss\sigma} h_{pp\pi} \cos\phi [(\epsilon_b - \epsilon_e)^{-3} + (\epsilon_b - \epsilon_e)^{-2} (\epsilon_b - \epsilon_a)^{-1}]. \quad (38)$$

Thus, since the energy denominators are negative, alignments are favored which have larger torsional angles. However, these give fairly weak contributions to the torsional potentials; using the above parameter sets, they are estimated to be on the order of  $10^{-2}$  eV per bond pair. In fact, the observed crystal structures of phosphorus reveal no well-defined torsional angles.

Much stronger effects are caused by the unbonded “lone-pair” ( $u$ ) orbitals in sulfur. These are oriented perpendicular to the occupied bonding orbitals. The effects of these are seen already at second order in perturbation theory. The bonding is illustrated schematically in Fig. 6. In Eq. (17), we note that  $\tilde{h}_{im}^{ae} = (1/\sqrt{2})h_{pp\pi}\sin\theta$ , where  $\theta$  is the angle between the two occupied orbitals. Thus the torsional potential becomes  $2h_{pp\pi}^2 \sin^2\theta / (\epsilon_u - \epsilon_a)$ . This favors  $90^\circ$  torsional angles. To obtain an approximate magnitude, we take  $h_{pp\pi} = 1.2$  eV and  $h_{pp\sigma} = 4.9$  eV from Ref. 16; assuming that

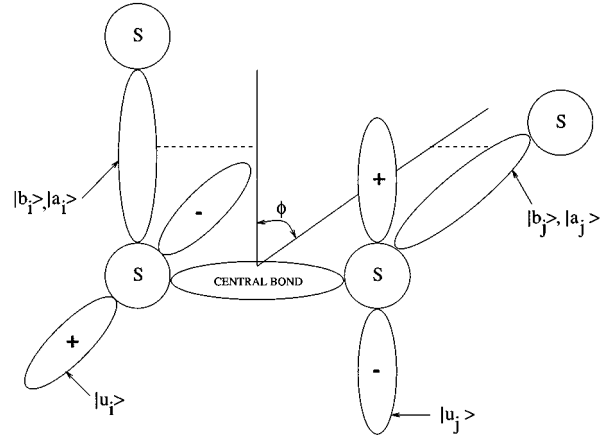


FIG. 6. Illustration of calculation of torsional potential for sulfur, using lone-pair orbitals.

$\epsilon_u - \epsilon_a = -h$ , we obtain an estimate of about  $1/2$  eV for the prefactor. The reasons for the greater strength relative to phosphorus are that the order in perturbation theory is lower, and that the energy denominator is smaller. Examination of the observed torsional angles in the many sulfur structures<sup>15</sup> reveals a mean value close to  $90^\circ$ , with most observed angles within  $10^\circ$  of the mean. In addition, the  $H_2S_2$  molecule, which may in some ways be thought of as a truncated piece of sulfur, has a torsional angle of  $90.6^\circ$ .<sup>18</sup> Thus the calculated torsional potential is consistent with the experiments.

The case of ethane has received considerable attention in the literature,<sup>10,19,20</sup> and it has generally been suspected that some type of interaction involving higher-lying  $d$  orbitals is necessary to reproduce the observed threefold rotational barrier. Our calculations confirm this belief. Because of the threefold hydrogen coordination of the carbons, it is necessary to have an angular dependence at least as rapid as  $\cos 3\phi$  in order to avoid cancellations of the contributions from the nine bond pairs. For the case of  $sp^3$  orbitals interacting with higher  $d$  orbitals, this results from the product of a  $\cos\phi$  factor coming from the  $\pi$  part of the  $bb$  or  $ab$  interactions, and a  $\cos 2\phi$  factor coming from the  $d$  interactions. The first piece [from Eq. (36)] is given by  $-(1/3)h_{pp\pi}\cos\phi$ . The  $d$  interactions, in order to obtain the  $\cos 2\phi$  behavior, must have  $\delta$  character with respect to the bond axis. It is convenient to choose the coordinates so that the bond is along the (001) axis and the right-hand ( $j$ ) ligand bond points in the (111) direction. Then the  $d$  orbital of  $\delta$  character that couples to this bond is the “ $xy$ ” orbital. From Ref. 14, we find that the coupling between the  $s$  state on the neighboring hydrogen and the  $xy$   $d$  orbital is  $-(1/\sqrt{3})h_{sd\sigma}$ , so that  $h_{nj}^{eb} = -h_{nj}^{ea} = -(1/\sqrt{6})h_{sd\sigma}$ . Then, because of the angular behavior of the  $xy$   $d$  orbital, the matrix elements on the left-hand ligand ( $i$ ) are  $h_{im}^{be} = -h_{im}^{ae} = -(1/\sqrt{6})h_{sd\sigma}\cos 2\phi$ . Furthermore,  $h_{mn}^{ee} = -h_{dd\delta}$ . Assembling these pieces in Eq. (24), we obtain the following effective bond-bond interaction (keeping only the  $\cos 3\phi$  part):

$$V(\phi) = -(2/9)h_{sd\sigma}^2 h_{dd\delta} h_{pp\pi} \cos(3\phi) (\epsilon_b - \epsilon_d)^{-2} \times [(\epsilon_b - \epsilon_d)^{-1} + (\epsilon_b - \epsilon_a)^{-1}]. \quad (39)$$



Because the energy-denominator terms are negative, this potential minimizes at a staggered configuration, consistent with the known geometry.<sup>18</sup> To obtain an estimate of the magnitude, we have from Ref. 16  $h_{pp\pi}=2.6$  eV and  $h=14.0$  eV. We do not have a reliable way of estimating  $h_{sd\sigma}$ ,  $h_{dd\sigma}$ , and  $\varepsilon_d$  in this case. However, since the  $d$  state is higher in energy than the valence states, we can assume its spatial extent to be fairly large, probably larger than that of the  $p$  state. To obtain a reasonable estimate, we will then take the  $\sigma$  couplings involving this  $d$  state to equal those of the  $p$  state at a corresponding distance. We then have  $h_{sd\sigma}=h_{sp\sigma}=11.8$  eV; the large value comes from the short hydrogen-carbon spacing (1.09 Å). To get the  $\delta$  couplings, we will use the “canonical band theory” rule<sup>21</sup> that  $h_{dd\delta}=h_{dd\sigma}/6$ , so that  $h_{dd\delta}=h_{pp\sigma}/6=1.8$  eV. For  $\varepsilon_d$ , we assume that the unoccupied  $d$  state is not too different in energy from the antibonding states, so that  $\varepsilon_b-\varepsilon_d=\varepsilon_b-\varepsilon_a=28.0$  eV. Then the prefactor of the  $\cos 3\phi$  term is 0.013 eV. Since all of the torsional bond interactions contribute equally, the energy difference between the staggered and eclipsed conformations is  $9\times[1-(-1)]\times 0.013$  eV = 0.24 eV, in comparison with the experimental value<sup>22</sup> of 0.13 eV. This indicates it is possible to get a sensible value of the torsional barrier with physically reasonable values of the parameters in the model. However, since previous analyses based on electrostatics<sup>19,20</sup> had obtained results of similar magnitude, we cannot definitely conclude that we have isolated the dominant piece here.

#### IV. CONCLUSION

The focus of this work has been on obtaining the basic theoretical underpinnings for the calculation of angular and torsional forces in well-bonded covalent systems. The examples of the preceding section show that the methodology

yields potential-energy functions that are physically sensible, and that differ in important respects from some empirical potentials. It should be possible to use these results to obtain force fields suitable for simulations of real molecules and solids. This will require addition of both “nonbonded” interactions, such as electrostatic terms, hydrogen bonding, and van der Waals interactions. Several procedures for doing this have already been worked out; see, for example, Ref. 12. In addition, it will be necessary to develop a way of obtaining detailed values of the coupling parameters in the Hamiltonian. The best procedure for doing this is probably to add some empirical fitting freedom, while using well-established properties of electronic structure to control the number of fitting parameters. Probably the first point to introduce fitting parameters would be in the overall strength of the electronic couplings, as given, for example, by  $h_{pp\sigma}$ . Using this as a fitting parameter, one could obtain the remaining  $s$ - $p$  parameters by standard universal dimensionless ratios as given, for example, in Ref. 16. This would introduce one parameter for each type of elemental bond that is present. To treat heteroatomic bonds, one could use one of several approximations in which the heteroatomic bond strength is given as an average of the homoatomic ones, or one could simply introduce extra fitting parameters for each heteroatomic bond. Even for a complex polymer such as a protein, this would introduce less than 20 adjustable parameters, which is much fewer than are typically used.

#### ACKNOWLEDGMENTS

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